MINERALOGICAL AND PETROLOGICAL STUDY OF MANTLE XENOLITHS FROM VICTORIA LAND (ANTARCTICA): INSIGHT OF THE ROLE OF THE AMPHIBOLE IN METASOMATIC PROCESSES
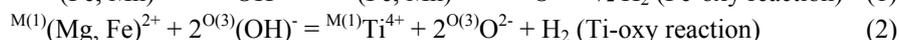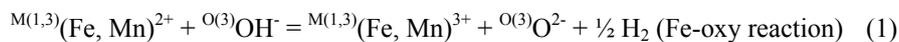
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INTRODUCTION

Hydrogen (OH, namely water) plays a fundamental role in physical and chemical properties of minerals and consequently influences the melting/enrichment processes occurring in the Earth upper mantle. Hydrogen could be storage as major constituent in hydrous minerals or as trace element in nominally anhydrous minerals (NAMs). Therefore it is important to better frame the behavior of water in hydrous and nominally anhydrous minerals, in order to understand the mechanisms to store water back into the mantle (*i.e.*, slab dehydration and/or melting), and to re-distribute the water in the various mantle tectonic settings, ultimately influencing the geochemistry of mantle metasomatism (*i.e.*, Coltorti *et al.*, 2007; Zanetti, 2009).

In anhydrous spinel bearing lithospheric mantle, the nature of melts/fluids responsible for mantle metasomatism is commonly constrained using geochemical features of clinopyroxenes (and glasses, if present) being the main repositories for trace elements (*i.e.*, Coltorti *et al.*, 1999, 2007; Ionov *et al.*, 2002). Recently, measurements of NAMs water contents, contribute to characterize the role of volatiles in potentially anhydrous mantle parageneses (*i.e.*, Hirschmann *et al.*, 2009; Bonadiman *et al.*, 2009; Warren & Hauri, 2014). Notwithstanding, precise information about the mantle/fluid circulation at mantle level can be obtained only if a hydrous phase (*i.e.*, amphibole and phlogopite) occurs in the mantle paragenesis.

Amphibole is the most common rock-forming hydrous mineral occurring in the mantle peridotites, as well as in magmatic and high-grade metamorphic lithologies. It is also believed to play a crucial role in the refertilization of lithospheric peridotites, and its occurrence has been frequently invoked in the mantle sources of alkali basalts and kimberlites to explain their geochemical features (Boettcher & O'Neill 1980; Halliday *et al.*, 1995; Martin, 2007). Moreover, being an important repository for trace elements, it represents an ideal tool for unrevealing the nature of melts and fluids migrating in the mantle wedge above subduction zones, as well as those circulating in the intraplate settings. In particular, calcic and sodic-calcic amphiboles, are characterized by a variable, but nearly ubiquitous, deficiency in H_2O and halogens content, namely a deviation from the nominal amphibole stoichiometry of 2(OH, F, Cl) apfu (Zanetti *et al.*, 1995, 1996; Hawthorne *et al.*, 1998; Hawthorne *et al.*, 2012). This feature implicitly requires the occurrence of O^{2-} at the O(3) site (*oxo* component), that can be locally balanced by two different exchange mechanisms:

$$^{M(1,3)}(Fe, Mn)^{2+} + {}^{O(3)}OH^- = {}^{M(1,3)}(Fe, Mn)^{3+} + {}^{O(3)}O^{2-} + \tfrac{1}{2} H_2 \text{ (Fe-oxy reaction)} \quad (1)$$

$$^{M(1)}(Mg, Fe)^{2+} + 2^{O(3)}(OH)^- = {}^{M(1)}Ti^{4+} + 2^{O(3)}O^{2-} + H_2 \text{ (Ti-oxy reaction)} \quad (2)$$

These two reactions are characterized by different Me: $^{O(3)}O^{2-}$ with 1:1 ratio for Fe-oxy reaction, and 1:2 ratio for Ti-oxy reaction. The decrease of the presence of the weak O(3)–H bond in oxo-amphiboles is, in principle, associated with an increase of their thermal and pressure stability. The knowledge of the amount of the *oxo* component and Fe^{3+}/Fe_{tot} ratio, also provide the estimate of the hydrogen fugacity (fH_2) and oxygen fugacity (fO_2) in mantle, permitting a deeper comprehension of the parameters governing the hydration processes. Moreover, the coexistence of amphibole with primary peridotitic parageneses allows to evaluate the chemical equilibrium among these phases as well as estimation of water activity under which amphibole crystallized.

It is well known that the kinetics of dehydrogenation reactions in minerals could be sufficiently fast during the ascent of mantle xenoliths, particularly regarding amphibole as many volatile-bearing phases (Dyar *et al.*, 1992, 1993; Peslier *et al.*, 2002; Oberti *et al.*, 2007), favoring the oxidation of Fe^{2+} (Frost & McCammon,

2008). This implies that Fe^{3+} concentrations in minerals are higher than those of the mantle region from which they were derived. For this purpose the Fe^{3+}/Fe_{tot} ratios in amphiboles can be compared with the estimated Fe^{3+}/Fe_{tot} ratio of the coexisting anhydrous phases. If the Fe^{3+}/Fe^{2+} equilibrium between hydrous and anhydrous minerals is verified, it can be assumed that *i*) amphiboles were not remarkably affected by H loss during the ascent and *ii*) fO_2, estimated on the basis of anhydrous mineral equilibria, can be extended to the entire parageneses (Bonadiman *et al.*, 2014).

Following the H_2O-buffering equilibrium proposed by Popp *et al.* (2006) the fO_2 can be estimated using the dissociation constant of water (K_w) from the reaction:

$$H_2 + \tfrac{1}{2}O_2 = H_2O \qquad (3)$$

where the aH_2O is obtained from amphibole dehydration equilibrium (Lamb & Popp, 2009), and fH_2 can be evaluated from the oxy-amphibole equilibrium of Popp *et al.* (2006).

From the above statement, it gathers that amphiboles structure and, in particular, its chemical composition are very sensitive to different physical-chemical conditions of crystallization. Therefore, the knowledge of amphibole crystal chemistry as well as its pressure dependence behavior, up to the breakdown, is a critical parameter governing the wet-solidus in the upper mantle, ruling both hydrous partial melting and the melt-peridotite reaction during the liquids migration.

Bonadiman *et al.* (2014) showed that amphibole with pargasitic and kaersutitic compositions, were stabilized by metasomatic processes in a low water activity mantle fragment, which in turn was not leading to enhance oxygen fugacity. Therefore they concluded that amphibole (*i.e.*, pargasite and kaersutite), being the main acceptor of H among the peridotite minerals, acted as a H–O buffer, preventing further fluid circulation.

Despite a large geochemical and crystal-chemical investigation on mantle amphibole has been done in the last decade (*i.e.*, Hawthorne *et al.*, 2012 and reference therein), a new geochemical characterizations of natural samples in relation to volatile (OH, F and Cl) contents and distribution among amphibole and anhydrous mantle minerals, shine a light on the potential water effects in the lithospheric processes.

AIM OF THE THESIS

This PhD thesis investigated the role of the amphibole in the upper mantle conditions, by means of detailed mineralogical and petrological study of mantle xenoliths from Harrow Peaks, Victoria Land (Antarctica).

The main goals were: *i*) the understanding of the amphibole's crystal chemistry at upper mantle conditions; *ii*) the broadening of the knowledge of the actual role of water circulation during metasomatic processes in the Antarctic region with particular attention to the nature of the migrating amphibole-forming melts/fluids; *iii*) the comprehension of the Antarctic lithospheric mantle redox conditions.

Lastly a methodological approach in evaluating the mineralogical quantitative composition of mantle peridotites was proposed, by comparing the results obtained from X-ray powder diffraction (by means of Rietveld refinements) and Mass Balance (MB) calculations. This methodological work aimed at providing an additional tool for a ubiquitous access to the volumetric distribution of minerals in mantle rocks.

ANALYTICAL METHODS

Amphibole crystals and whole rock samples were studied with different analytical techniques in order to evaluate their structural, chemical, and mineralogical composition.

Amphiboles were studied in detail by a chemical and structural point of view. Quantitative chemical analyses of amphiboles were carried out using a CAMECA SX-50 electron microprobe (WDS mode, accelerating voltage 15 kV, beam current 15 nA, beam size 1 μm) and Secondary Ion Mass Spectrometry (SIMS). SIMS analyses on selected areas of the amphibole crystals were performed with a CAMECA IMS 4f ion microprobe. A -12.5 kV accelerated $^{16}O^-$ primary beam was used with 5 nA current intensity, < 8 μm Ø

diameter. Well characterized amphibole crystals (Ottolini *et al.*, 1995) were chosen to convert H^+ current intensity into H_2O wt.% concentration. The Mössbauer spectra were collected in order to establish the Fe^{3+}/Fe_{tot} ratio. The data collection was performed at room temperature in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal 370 Mbq ^{57}Co high specific activity source in a 12 μm thick Rh matrix. Mössbauer spectra were fitted to two Lorentzian doublets and the usual constraints were applied to all doublets (equal component areas and widths) by using the program MossA (Prescher *et al.*, 2012).

Single-crystal X-ray diffraction (SCXRD) was carried out using a Bruker Smart Breeze single-crystal diffractometer equipped with an air-cooled CCD detector. Intensity data were integrated and corrected for Lorentz, polarization, background effects, and absorption. Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). The occupancies of the cation sites were refined using the following scattering curves: $M(1)$, $M(2)$, $M(3)$ sites: Mg *vs.* Fe; $M(4)$ site: Ca *vs.* □; $M(4')$: Fe *vs.* □; $A(m)$ and $A(2/m)$ sites: Na *vs.* □. The site scattering at the $T(1)$ and $T(2)$ sites indicated that they are full-occupied by (Si, Al).

In order to evaluate the mineralogical and chemical composition of a set of mantle peridotites from Victoria Land (Antarctica; Gentili *et al.*, 2015), the whole rock analyses by means of modal (mineralogical quantitative analysis) and chemical composition were performed by applying X-Ray Powder Diffraction (XRPD), X-Ray fluorescence (XRF) and electron microprobe (EMPA).

The XRPD analysis was performed on powdered samples at room temperature using a Bruker D8 Advanced diffractometer in reflection mode with Bragg-Brentano geometry. Cu *K*α radiation (λ = 1.5406 Å) was used with a Ge primary monochromator with a fixed divergence slit of 0.2°. Intensities were collected using a linear PSD detector (Bruker Lynx-Eye) with opening angle 3.3° over a 5-110° 2θ range. The XRPD data was refined using the Rietveld method (Rietveld, 1969) by means of TOPAS software (Cheary & Coelho, 1992; Cheary *et al.*, 2004). The Mass Balance (MB) calculations were performed by using least-squares procedure (Marthy, 1973). The results were obtained by coupling major elements compositions *i*) of bulk rock, carried out by XRF with those *ii*) of minerals from EMPA.

OXO-AMPHIBOLES IN MANTLE XENOLITHS FROM HARROW PEAKS (ANTARCTICA)

The amphiboles were found as the most widespread hydrous metasomatic phase in spinel-bearing lherzolites, harzburgite, and wehrlite xenoliths from Harrow Peaks (HP), Northern Victoria Land (Antarctica). They occurred both in veinlets and disseminated in the peridotite matrix (preferentially associated with clinopyroxene and spinel grains). In order to understand the amphibole's crystal-chemistry at upper mantle conditions and to broaden the knowledge of the actual role of water circulation during metasomatic processes in the Antarctic region, four amphibole crystals were fully characterized, by means of single-crystal X-ray diffraction, electron microprobe analysis, secondary ion mass spectrometry, and micro-Mössbauer spectroscopy.

Compositionally, they present relatively low Mg# values (69.3-84.1) and high TiO_2 contents (2.74-5.30 wt.%). FeO_{tot} contents range from 3.40 to 6.90 wt.% and the Fe^{3+}/Fe_{tot} ratios (0.53-0.66%), revealing anomalously high Fe_2O_3 contents (2.34-4.52 wt.%). The amount of O^{2-} at the O(3) site (0.984-1.187 apfu), together with the anomalously high Fe_2O_3 contents, testify for the presence of the *oxo* component in the Harrow Peaks amphiboles. The volatile content is mainly represented by H_2O (0.70-1.01 wt.%) and minor amounts of F and Cl, (0.04-0.24 wt.% and 0.03-0.08 wt.%, respectively; Table 1). The coexistence of amphibole with the primary peridotite phases allowed to investigate the intensive parameters that control the amphibole formation.

The aH_2O values were calculated at 1.5 GPa by dehydration equilibrium equations written as H_2O-buffering equilibria among end-member components of amphibole and coexisting peridotitic phases (Lamb & Popp, 2009). Three out of four HP amphibole-bearing peridotites record aH_2O values from 0.122 to 0.335; one sample has aH_2O remarkably higher (0.782) and close to the ideal H_2O saturation. These values are not unexpected, due to the predominance of the *oxo* components in the amphiboles.

Table 1 - Chemical formulas of HP amphiboles

Sites		HP121	HP124	HP143	HP164	Sites		HP121	HP124	HP143	HP164	Sites		HP121	HP124	HP143	HP164
T	Si	6.137	6.198	6.182	6.089	**B**	Ca	1.696	1.829	1.763	1.726	**W**	OH	0.820	0.989	0.898	0.682
	Al	1.863	1.802	1.818	1.911		Mn	0.007	0.006	0.007	0.014		F	0.042	0.020	0.038	0.111
	Tot.	8.000	8.000	8.000	8.000		Fe^{2+}	0.158	0.165	0.230	0.257		Cl	0.017	0.007	0.012	0.020
C	Mg	3.699	3.738	3.742	3.383		Mg	0.139	0.000	0.000	0.000		Tot.	0.879	1.016	0.948	0.813
	Al	0.406	0.373	0.470	0.439		Tot.	2.000	2.000	2.000	1.997		O^{2-}	1.121	0.984	1.052	1.187
	Ti	0.462	0.303	0.377	0.582	**A**	Na	0.729	0.919	0.854	0.816						
	Cr	0.175	0.181	0.105	0.010		K	0.131	0.082	0.131	0.179						
	Fe^{3+}	0.258	0.376	0.284	0.497		Ca	0.180	0.125	0.135	0.000						
	Fe^{2+}	0.000	0.029	0.022	0.089		Tot.	1.040	1.126	1.120	0.995						
	Tot.	5.000	5.000	5.000	5.000												

The HP fO_2 values, determined by the olivine-spinel-orthopyroxene oxygeobarometer (fO_2 between -1.77 and + 0.01 ΔQFM), were remarkably different from those calculated on the basis of the amphibole dehydration equilibrium (Popp *et al.*, 2006; Lamb & Popp, 2009), and the application of the water dissociation reaction (fO_2 between from -2.60 to +6.8 ΔQFM; Fig. 1).

The high aH_2O and the extremely high fO_2 values, determined by the oxy-amphibole equilibrium with respect to the redox conditions recorded by the co-existing anhydrous minerals (close to QFM buffer), reveal that: *i*) the amphibole is not equilibrated with the peridotite mineral assemblage; *ii*) the circulation at mantle level of a water-rich, amphibole-forming, high oxidizing fluid/melt can be envisaged; *iii*) the studied mantle region is, in principle, an halogen-rich zone, preferentially incorporated in olivine and/or pyroxenes instead of amphibole.
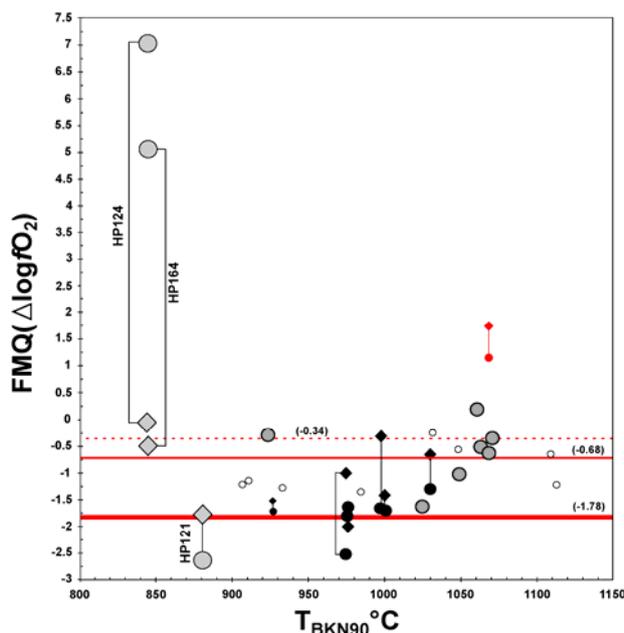

Fig. 1 - (Δlog$fO2$)FMQ = $fO2$ relative to the buffer reaction FMQ calculated with Ballhaus *et al.*, (1991) oxygeothermobarometer (large grey diamonds) and with Popp *et al*. (2006) oxy-amphibole equilibrium (large grey circles) *versus* the temperature calculated with the formula TBKN90 of Brey & Köhler (1990). For other symbols refer to Bonadiman *et al*. (2014).

A possible scenario interprets the amphibole-forming reaction as a relatively recent process, far from having reached a potential equilibrium with the peridotite matrix. The amphibole seems to be formed by the precipitation of migrating hydrous rich fluid/melts with a negligible contribution of the peridotite system.

FERRI-KAERSUTITE, A NEW *OXO*-AMPHIBOLE

Ferri-kaersutite, ideally $NaCa_2(Mg_3TiFe^{3+})(Si_6Al_2)O_{22}O_2$, is a new *oxo*-amphibole from Harrow Peaks, Northern Victoria Land, Antarctica. It occurs as brown prismatic crystals, up to 200 μm in length, with a vitreous luster, and a perfect {110} cleavage. Ferri-kaersutite is associated with forsterite, diopside, and Cr-bearing spinel. Chemical analyses, by a combination of electron microprobe, SIMS, and ^{57}Fe Mössbauer spectroscopy, gave the following results (in wt.%): SiO_2 41.69, TiO_2 5.30, Al_2O_3 13.65, Cr_2O_3 0.09, Fe_2O_3 4.52, MgO 15.54, CaO 11.03, MnO 0.11, FeO 2.83, Na_2O 2.88, K_2O 0.96, H_2O 0.70, F 0.24, Cl 0.08, O = (F, Cl) -0.12, sum 99.50. On the basis of 24 anions per formula unit, the formula is $(Na_{0.816}K_{0.179})_{\Sigma=0.995}(Ca_{1.726}Fe^{2+}_{0.258}Mn_{0.014})_{\Sigma=1.998}$ $(Mg_{3.383}Fe^{2+}_{0.088}Ti_{0.582}Fe^{3+}_{0.497}Al_{0.439}Cr_{0.011})_{\Sigma=5.00}(Si_{6.089}Al_{1.911})_{\Sigma=8.00}O_{22}[O_{1.187}(OH)_{0.682}F_{0.111}Cl_{0.020}]_{\Sigma=2.00}$.

Ferri-kaersutite is monoclinic with space group $C2/m$. Its unit-cell parameters are: a = 9.8378(8), b = 18.0562(9), c = 5.3027(4) Å, β = 105.199(9)°, V = 908.99(13) Å^3, Z = 2. The five strongest reflections in its X-ray powder diffraction pattern [d in Å (relative visual intensity, hkl)] are: 2.707 (s, 151), 3.115 (ms, 310), 8.4 (s, 110), 3.379 (ms, 131), 2.598 (ms, 061). The crystal structure of ferri-kaersutite has been refined on the basis of 1783 observed reflections $[F_o > 4\sigma(F_o)]$ with a final R_1 = 0.038.

The relatively large equivalent isotropic displacement parameter at $M(1)$, with respect to those at $M(2)$ and $M(3)$ sites, together with the short $M(1)$–$O(3)$ distance, suggest the occurrence of Ti^{4+} at the $M(1)$ site, whereas the small octahedral distortion at this site suggests a low Fe^{3+} occupancy. This element is mainly hosted at the $M(2)$ and $M(3)$ sites (Fig. 2).
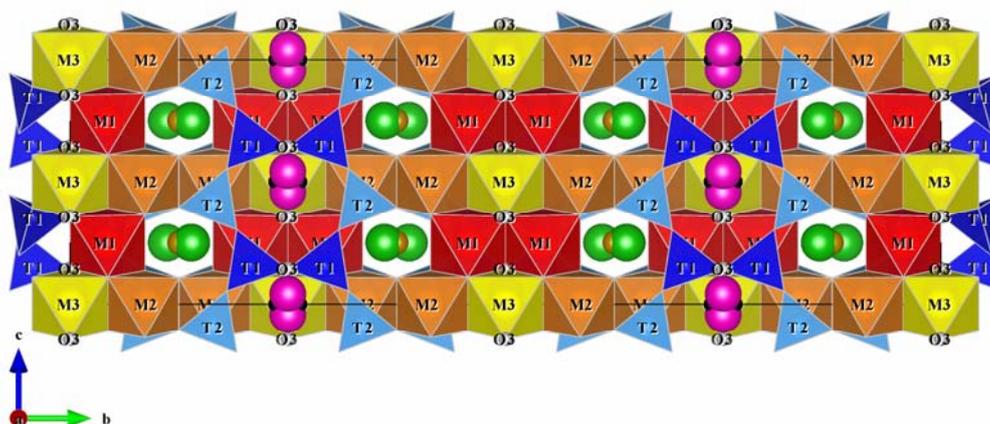

Fig. 2 - The $C2/m$ structure of ferri-kaersutite along (100) plane. Polyhedra: $T(1)$ blue, $T(2)$ light blue, $M(1)$ red, $M(2)$ orange, $M(3)$ yellow, $M(4)$ light green, $M(4')$ brown, $A(2)$ pink, $A(m)$ black.

The occurrence of amphiboles in the magma source region is notably relevant. The melting of Ti-rich amphibole in the lithosphere and subsequent degrees of melt/host peridotite reactions are able to produce melts which account for the compositional spectrum ranging from extreme alkaline lavas to the most common alkaline basalts. In particular, when this amphibole is formed by reaction between a peridotite matrix and metasomatic melts/fluids with high Fe^{3+}/Fe_{tot} ratio, its subsequent melting can influence primary volatile contents and ultimately magma rheology.

MASS BALANCE *VS.* RIETVELD REFINEMENT TO DETERMINE THE MODAL COMPOSITION OF ULTRAMAFIC ROCKS

The estimation of mineral quantities in a multi-component system, as rocks are, constituted the base of reasoning for any mineralogical and petrological study. For mantle peridotites, indeed, analyses of the relative

mineral percentages were essential to apply any geochemical model (both major and trace elements) to evaluate melting and enrichment events (Ionov *et al.*, 2010; Kelemen *et al.*, 1997; Niu, 2004).

This methodological work aimed at applying the Rietveld refinement method to XRPD spectra in order to determine the mineralogical assemblages of ultramafic rocks. The results were compared to those obtained by MB calculations, a least squares method that reduces major element chemical analyses to the whole rock composition. This methodological work was carried out in five hydrous and anhydrous mantle xenoliths from Northern Victoria Land, Antarctica.

The intrinsic goodness of the XRPD and MB results, evaluated by with R_{wp} and r^2 respectively, showed similar values of modal compositions. Independent of the mineralogy (amphibole-bearing and amphibole-free) and textures (fine to coarse grained), good agreement (< 2%) was observed for modal contents lower than 10%, whereas a discrepancy of up to 10% was recorded for phase abundances higher than 70%. The comparison of the two methods has allowed us to demonstrate that the Rietveld method is applicable even when limited amount of material (< 1 g) is available, and the "classical" chemical approaches (XRF and EMPA) cannot be applied. Moreover, it provides information not only on rock mineral concentrations (wt.%), but also gives supplementary information on crystallographic data (*i.e.*, mineral crystallite size, mineral lattice parameters, density, and site occupancies; Table 2).

Table 2 - XRPD and MB results (expressed as wt.%). Errors are reported in parentheses.
For MB errors are calculated as standard deviation for 10 cycles each of 100 iterative runs.

	BR154G		BR154H		HR1		HR9		OV1	
	XRPD	MB	XRPD	MB	XRPD	MB	XRPD	MB	XRPD	MB
OL	64.6(4)	66.7(4)	77.5(6)	86.5(4)	60.9(4)	66.0(2)	65.8(4)	76.0(2)	66.4(4)	62.5(6)
OPX	23.2(4)	21.5(3)	14.5(3)	6.7(2)	24.0(3)	19.5(2)	20.0(3)	12.5(2)	na	na
CPX	8.1(3)	6.8(4)	5.1(3)	3.2(3)	12.3(3)	12.0(2)	12.0(3)	8.5(2)	27.8(3)	31.5(5)
AMPH	2.6(3)	1.0(4)	0.9(3)	1.2(2)	na	na	na	na	na	na
SPIN	1.5(2)	4.0(4)	1.9(5)	2.4(3)	2.8(3)	2.5(3)	2.1(3)	3.0(1)	5.8(3)	6.0(4)
R_{wp}	3.385		4.131		5.956		5.692		4.108	
r^2		0.949		0.969		0.578		0.957		1.000

On the other hand, the MB procedure provides direct chemical information of both bulk rock and minerals, but requires a large amount of material (*i.e.*, for XRF at least > 1 g of material is needed). Dealing with MB procedure, problems can occur if accessory minerals cannot be identified in thin sections, which are, however, part of the whole-rock analysis. Besides, the strength of XRPD, if compared with all the suitable methods for the quantitative mineralogical identification, is to provide direct information about the physical properties, and mineral site occupancies that could indirectly give a mineral chemical composition.

CONCLUSIONS

The crystal chemical study of the amphiboles from Harrow Peaks showed a predominant *oxo* component (namely $^W O^{2-} > {}^W (OH+F+Cl)^-$), unusual (peculiar) for mantle amphiboles. The low volatiles contents, (in particular OH contents) of amphiboles were accompanied by high aH$_2$O (up to 0.8, close to the water saturation) and extremely high fO$_2$ values (up to 7 log units above QFM buffer) determined by the oxy-amphibole equilibrium. These values, with respect to the redox conditions recorded by the co-existing anhydrous minerals (close to QFM buffer), revealed that amphiboles were not equilibrated with the peridotite mineral assemblage. The amphibole-forming reaction was probably a relatively recent process, far to having reached a potential equilibrium with the peridotite matrix, with amphiboles that (chemically) seems to be formed by precipitation of migrating hydrous rich fluid/melts with negligible contribution of the peridotite system.

Within the crystal chemical study of the amphiboles from Harrow Peaks, a new member of the *oxo-*amphibole group, ferri-kaersutite, was discovered and fully characterized. Below are summarized the main features:

i) the relatively large equivalent isotropic displacement parameter at $M(1)$, with respect to those at $M(2)$ and $M(3)$ sites, together with the short $M(1)$–$O(3)$ distance, suggest complete ordering of Ti^{4+} at the $M(1)$ site, whereas the small octahedral distortion at this site suggests a low Fe^{3+} occupancy. This element was mainly hosted at the $M(2)$ and $M(3)$ sites;

ii) Ferri-kaersutite shows the preferential partitioning of Al at the $T(1)$ site; indeed this site has an Al/(Al+Si) atomic ratio close to 0.45, suggesting a crystallization temperature of 850 ± 50 °C;

iii) the formation of ferri-kaersutite suggests that the Fe^{3+}/Fe_{tot} ratio of the metasomatic silicate melts was high, and/or that the volatile rich melt/fluid percolated through and reacted with the peridotite, concentrating Fe^{3+} and C-O-H volatile species, and increasing Fe^{3+}/Fe_{tot} until the crystallization of ferri-karsutite.

Finally, the comparison of the strengths and weaknesses of the XRPD by applying the Rietveld method and the MB calculation to determine the mineralogical assemblages of ultramafic rocks, revealed that Rietveld quantitative XRPD could provide a screening tool for the selection of samples which are suited for detailed microanalysis (Gonzales *et al.*, 2003) and, of course, a useful tool to identify mineralogical quantitative analysis and amorphous content when limited amounts (< 0.5 g) of material are available. On the other hand the MB procedure provided direct chemical information of both bulk rock and minerals, but required a large amount of material (*i.e.*, for XRF at least > 1 g of material is needed), although dealing with MB procedure, problems can occur if accessory minerals cannot be identified in thin sections, which are, however, part of the whole-rock analysis.

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